NREL Nanoscience & Nanotechnology

Meeting 21st Century Energy Challenges

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Many futurists, scientists, and technologists believe that nanotechnology in the 21st century could prove to be as socially transformative as running water, antibiotics, plastics, or semiconductors have been. Nanotechnology will have a crucial impact on everything from cars, health, and security to computers and materials science. Serious projections for it include building materials that can sense weather and change properties accordingly, lightweight materials far more durable than steel and hundreds of times stronger, computers that are orders of magnitude faster than today's, and nanoscale biosensors that can be injected into blood streams to diagnose and treat illnesses.

At NREL, we see the 21st century also as a century of new energy concepts and nanotechnology as a technology that will enable sustainable, benign, efficient, and inexpensive energy. In fact, when applied to energy, the impact of nanotechnology may turn out to be as great as that brought about by civilization's turn to fossil fuels, which resulted in the industrial revolution. To put this in perspective, today the world consumes about 13 terawatt-years (TW-yrs) of energy per year. (A terawatt is 10^{12} W.) But according to the DOE's Basic Energy Sciences Advisory Committee, the world's energy consumption will more

than double by 2050. And papers from Hoffert et al. published in the journal *Nature* show that, if we are to meet this demand while stabilizing the CO_2 in the atmosphere at a reasonable level—such as 550 parts per million, or twice the pre-industrial level—at least 100% of this new energy would have to come from non-CO_2 generating sources. This is a daunting challenge that will take a major effort and important breakthroughs in energy technology and science. Nanotechnology will help meet this challenge.

Nanotechnology deals with materials and phenomena on the scale of 1 billionth (10^{-9}) to several tens of billionths of a meter. This is larger than the atomic scale, smaller than the bulk scale, and about the size of some molecules, including DNA and proteins. But the nanoscale is not simply a move toward miniaturization. It is a scale at which properties are qualitatively different from those of bulk materials. This includes electrical, material, and optical properties. Because of these properties and because of new techniques, we can design and construct new materials and systems with attributes and capabilities not found in bulk material or in nature.

NREL's Early Start

It is because of these qualitatively different properties and their applications to renewable energy and energy efficiency that NREL has long been studying nanotechnology. In its early efforts, NREL explored specific nanoscale components and materials, how to make them, their characteristics and properties, the mechanisms underlying those properties, and how to understand those properties and predict others.

For example, in 1983, shortly after the Laboratory first opened its doors, NREL began making and studying colloidal quantum dots (QDs). NREL researchers were among the first to report on the quantization effects of nanosized semiconductor particles—a phenomenon whereby emission and absorption spectra vary dramatically with the size of the nanoparticle (see sidebar "Quantum Confinement: Shifting Toward the Blue").

Starting in 1991, NREL's Solid-State Theory Group began fundamental explorations of QDs, developing a theory that enables them to model optical and electronic properties of neutral and charged QDs and QD arrays. NREL also began its study of single-wall carbon nanotubes in 1993, the same year their existence was discovered, and of nanoparticle precursors in 1995.

Nanoparticle Precursors. Nanoparticle precursors are typically metal or semiconductor material crystalline structures less than 20 nm in diameter and that are used to form a precursor state for a macroscopic device. In the process of forming the macroscopic device, the nanoscale nature of the starting material is altered or destroyed. Althou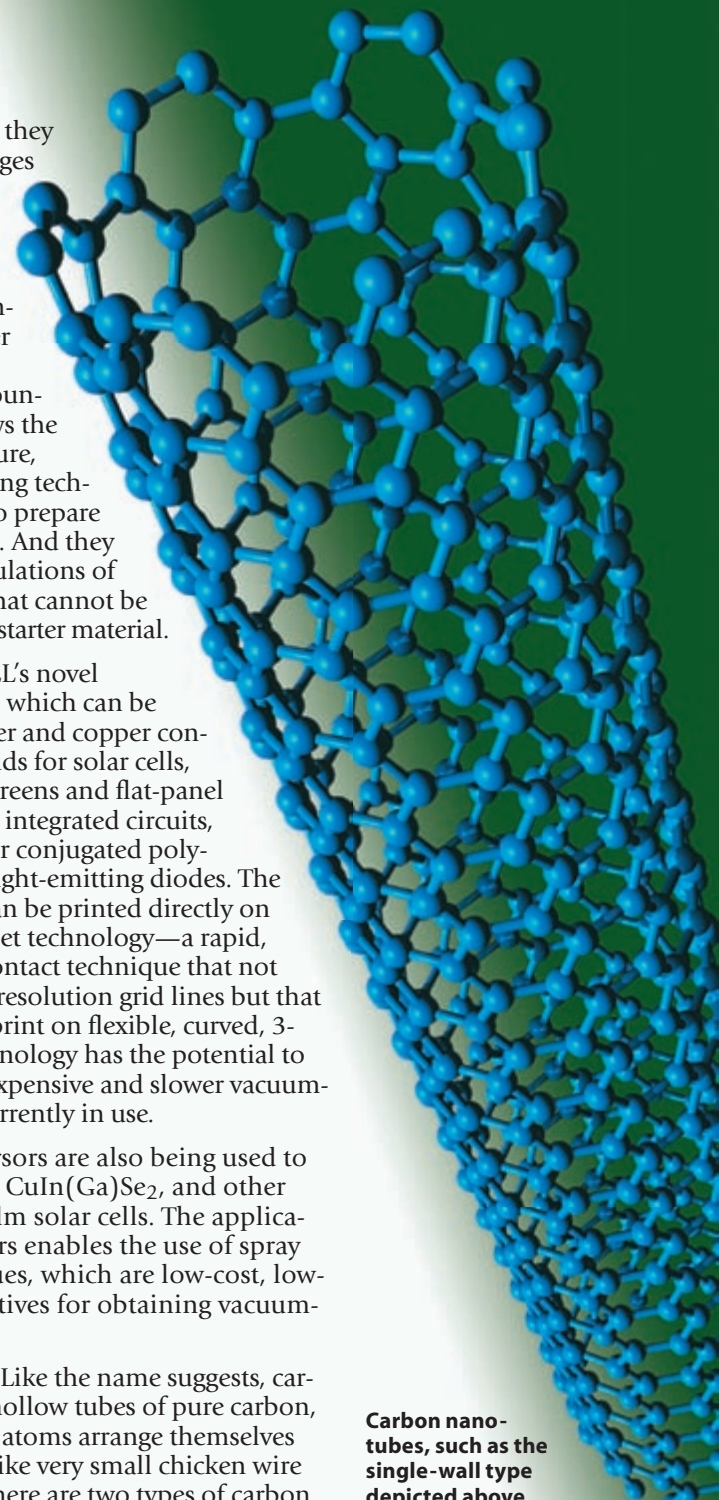gh nanoparticle precursors do not generally exhibit quantization effects, they have several advantages over other starting materials. They can be easily and inexpensively prepared using colloidal chemistry. They have lower melting points than their macroscopic counterparts, which allows the use of low-temperature, inexpensive processing techniques with which to prepare macroscopic devices. And they allow versatile formulations of solutions and inks that cannot be obtained with larger starter material.

One example is NREL's novel organometallic inks, which can be used to produce silver and copper contacts and metallic grids for solar cells, contacts for touch screens and flat-panel displays, busbars for integrated circuits, and metallic grids for conjugated polymer solar cells and light-emitting diodes. The grids and contacts can be printed directly on the device using inkjet technology—a rapid, atmospheric, non-contact technique that not only produces high-resolution grid lines but that also can be used to print on flexible, curved, 3-D surfaces. This technology has the potential to supplant the more expensive and slower vacuum-based technology currently in use.

Nanoparticle precursors are also being used to make films of CdTe, CuIn(Ga)Se$_2$, and other materials for thin-film solar cells. The application of the precursors enables the use of spray deposition techniques, which are low-cost, low-temperature alternatives for obtaining vacuum-quality materials.

Carbon Nanotubes. Like the name suggests, carbon nanotubes are hollow tubes of pure carbon, in which the carbon atoms arrange themselves in hexagonal rings, like very small chicken wire rolled into a tube. There are two types of carbon nanotubes: single-wall nanotubes (SWNTs), comprised of a single shell of carbon atoms, approximately 1–2 nm in diameter and several microns long; and multi-wall nanotubes (MWNTs), comprised of multiple concentric nested tubes, with an outside diameter of several tens of nanometers.

NREL is one of the few labs to use all four of the known major methods for synthesizing nanotubes. The first one used at NREL was the same method used to discover SWNTs: arc-discharge. Subsequently, NREL developed a laser vaporization technique in which a graphite target is irradiated with laser pulses. The pulses evaporate the graphite target to produce a variety of reactive carbon intermediate structures that, when quenched

Carbon nanotubes, such as the single-wall type depicted above, exhibit properties that make them attractive for a wide variety of applications. On the opposite page are quantum dots being aligned using a cellulosome polymer; the De-Broglie wavelength equation for matter waves; a π-conjugated polymer structure; and a C$_{60}$ "buckyball."

in the presence of the appropriate catalyst, form the nanotubes. The diameter of the SWNTs can be manipulated by controlling the pulse power of the laser—the higher the pulse power, the smaller the carbon fragments and the smaller the diameter of the tubes. NREL has also developed chemical vapor deposition methods to form SWNTs using methane as a feed gas. This process, though not as controllable as the laser-based one, promises to be amenable to low-cost, large-scale manufacture of nanotubes. Recently, NREL developed a hot-wire chemical vapor deposition technique, in which a hot wire filament in a vacuum chamber is heated in a carbon-bearing gas, such as methane. As the gas decomposes, it frees the carbon atoms, which recombine to form multi-wall nanotubes.

Carbon nanotubes have interesting properties that make them valuable for a variety of applications. For example, they have extremely high tensile strength and could be used in composites for making armor, space crafts, or lightweight, resilient cars (important for energy-efficient transportation). Multi-wall nanotubes have interesting field emission characteristics, prodigiously emitting electrons at low voltage from their tips; this gives them great potential for use in solid-state lighting and flat-plate displays.

Because SWNTs have small diameters, typically less than 2–3 nm, quantum effects are readily apparent. For example, electrons in a SWNT can maintain their quantum state and travel ballistically along the nanotube, electrons and phonons are strongly coupled, and exciton binding energies exceeding 1 eV have been predicted. In addition, SWNTs can be made with either semiconductor or metallic properties, depending on how the two-dimensional sheets of graphite are rolled up. The semiconductor variants exhibit strong photoluminescence. These properties make SWNTs ideal candidates for wires that carry high current and for applications in which highly conductive and high-surface materials

are required, such as in fuel cells, ultracapacitors, and organic photovoltaics. They are also strong candidates for supports for other nanoscale catalysts. Nanotubes can also be used as interconnects in highly efficient electronic switches, for photoactive media in transistors or solar cells, and as conduits for transferring charge carriers between quantum dots.

One characteristic of great interest to NREL is the ability of SWNTs to reversibly store lithium ions and hydrogen gas. This capability is particularly important for use in lithium batteries which, for energy storage, have the advantages of high energy density, low maintenance, long life, light weight, and design flexibility. For hydrogen, nanotubes show promise of safe, lightweight, high-density storage, which may prove to be particularly valuable for the future hydrogen economy—in which abundant, benign hydrogen, along with hydrogen fuel cells, will supply energy for heating, cooling, electricity, industrial processes, and transportation. Carbon nanotubes and related carbon-based materials are among our best bets for meeting the DOE goal to develop systems that will store enough hydrogen for our cars and trucks to be driven more than 300 miles between fill-ups without affecting cargo or passenger space. (For more on hydrogen storage with SWNTs, see the article "New Horizons for Hydrogen" in the *National Renewable Energy Laboratory 2003 Research Review*.)

Quantum Dots. Quantum dots are small semiconductor nanocrystals with diameters that range from about 2 to 10 nm and that typically contain from hundreds to thousands of atoms. Because of their small size, quantization effects become important. Quantum dots confine electrons to discrete, widely separated energy levels, which gives the dots optical and electronic properties that are dependent on the size of the dots and the material out of which they are made (see sidebar "Quantum Confinement: Shifting toward the Blue"). This makes them particularly valuable for solar cells, as a pathway toward high efficiency and low cost.

NREL makes several types of QDs, including CdSe, CdS, CdTe, InP, InAs, PbSe, and PbS. We

To exist, an electron in a confined space (such as in a spherical quantum dot) must have an associated wavelength that is equal to the inside circumference of the confining space or a whole number fraction thereof (½, ⅓, ¼, etc.). The smaller the dot, the shorter the wavelength that fits, the higher the energy of the electron. Hence, the absorption and emission spectra shift to the blue (higher energy) for smaller dots.

Quantum Confinement: Shifting toward the Blue

A salient feature of QDs is that they can be tailored to absorb or emit specific wavelengths of light simply by changing the size of the dot. Compared with the bulk material, the light spectra emitted or absorbed by QDs will shift to the blue (greater energy or shorter wavelength); the smaller the dot, the greater the shift. The shift is dependent on the size of the dot and the type of material.

Why does such quantized absorption or emission happen? Fundamental to quantum physics is the concept of the wave/particle duality of matter. For example, an electron can be thought of either as a particle or as a wave moving through its space. In bulk material, electrons exist at many energy levels—in fact, a continuum of energy levels in

valence and conduction bands—because of the numerous atoms in the material. (No electron, however, can exist in the forbidden region between the top of the valence band and the bottom of the conduction band.) But, as the size of a material approaches the nanoscale, it starts to confine the energy levels at which an electron may exist.

To see why, think of an electron as a wave and the QD as a sphere with a diameter approximately the size of the Bohr radius, which confines the electron (see also sidebar "Excitons"). In such a confinement, the electron has to travel within the inside circumference of the sphere so that its wavelength does not destructively interfere with itself. This means that the confining circumference must be equal to the electron wavelength or some whole number multiple of

make dots in two ways (both of which can be self-organizing): epitaxial growth and colloidal chemistry. Epitaxial growth is the growth of crystals of one semiconductor material on the surface of another, in which both materials have the same structural (lattice) orientation. NREL researchers are exploring a particular version of epitaxial growth known as Stranski-Krastanow growth, in which a mismatch of the lattices produces strains between the two materials causing islands to form. Most of the deposited material will accumulate on the islands, thus forming a matrix of QDs, whose size can be directed by controlling the growth conditions. To make these QDs, researchers use either of two well-known vacuum technologies: molecular beam epitaxy or metalorganic chemical vapor deposition.

Colloidal chemistry, however, is NREL's primary method of making quantum dots. This is an inexpensive way to grow the dots, requiring only the right chemicals, low-cost equipment, and room-temperature processing. Colloids are ultra-fine particles suspended in a liquid solution—colloids are formed by not having the solute molecules break up into atoms and thus dissolve. The formation of QDs involves a chemical reaction between a metal ion (such as indium) with a molecule that donates a different ion (such as phosphide). The size of a QD is manipulated by controlling the concentration of the reactants, the medium in which they react, the temperature of the reaction, and the length of the reaction.

The trick is to keep QDs from agglomerating when they have reached the desired size. This is done generally by having the reaction take place in the presence of organic molecules that act as surfactants and coat the surface of the nanoparticles—the organic molecules stop the crystals from clumping together.

Nanorods. These are semiconductor rods that are typically on the order of 2–10 nm in diameter and tens to several hundreds of nanometers long. It is the small diameter that promotes quantization effects and gives them similar characteristics to quantum dots. Nanorods, however, are unconfined in one direction, and charge carriers are free to move along the length of the rod. Nanorods of some materials can be grown using colloidal chemistry in a similar manner to QDs, except that growth is promoted along one axis and retarded along the other two axes via appropriate control of the growth solution, growth kinetics, and surfactants. There are other methods being explored to grow nanorods, such as via nucleation in a supersaturated solution. Nanorods of particular interest to NREL include CdS, InP, PbSe, PbS and several oxides, such as ZnO and TiO_2. Like QDs, nanorods are particularly promising for use in solar cells (also see sidebar "Printing Polymer Solar Cells").

Nanostructured Solar Cells

NREL's early explorations are paying off. They have given us the ability to make and understand nanoscale components. In addition, our use of sophisticated measurement techniques— such as atomic force microscopy, scanning tunneling microscopy, transmission electron microscopy, near-field scanning optical microscopy, and more—have enabled us to image what is occurring on the nanoscale and to measure the material, optical, and electronic properties of these nanocomponents. This ability to make, measure, image, and model nanoscale components and systems has given us the tools with which to proceed to the next important step— to build composite devices and systems with new properties that will allow us to do new things.

Imaging with atomic force microscopy shows QDs (conical shaped) attached to an individual SWNT (thin wire shape), demonstrating the ability nanotubes have to organize quantum dots.

Among these new composite systems is nanostructured solar cells. Solar PV cells represent an extremely promising technology for supplying large amounts of non-carbon energy in the future. However, to meet that promise—to be used on the massive scales needed—PV electricity has to be competitive with the least-costly alternative. This means the present cost of PV electricity has to be decreased by at least three- to fivefold to 6¢/kWh, or less. Plus, if PV electricity is to be used to competitively produce hydrogen (via the electrolysis of water) on a central-station scale for the future hydrogen economy, the cost has to be reduced by at least another factor of two to three.
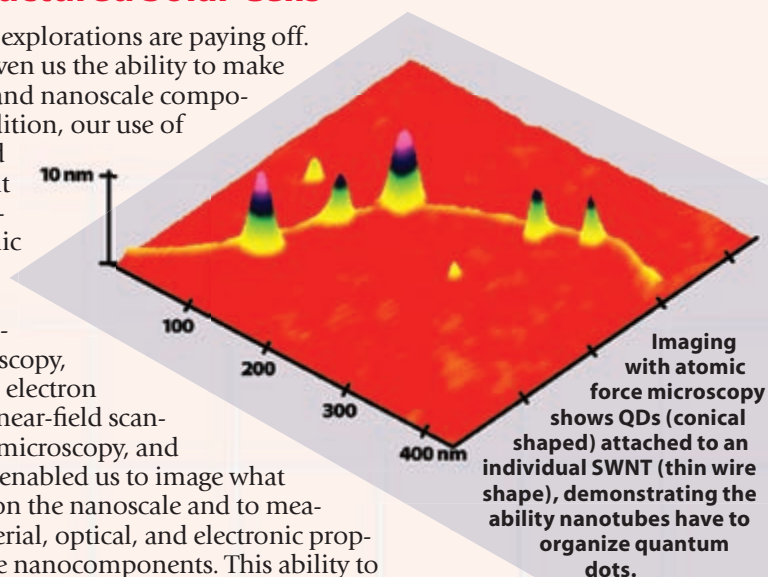
the wavelength. If it is other than this, the wavelength would interfere with itself and destroy its possibility of existing.

Thus, only certain (quantized) wavelengths can exist in such a confinement. The shorter the diameter of the confinement, the shorter the wavelength of the electron. And because energy is inversely proportional to wavelength (directly proportional to frequency), the smaller the QD, the smaller the allowable wavelength, the greater the frequency, and the bluer the associated photon emission or absorption spectra.

The same phenomenon holds for nanorods. But in this case the rod is to be likened to a cylinder and the confinement space dictated by the diameter of the cylinder.

Today, PV electricity costs about 18–30¢/kWh, depending on the application and its scale. The technology that has dominated the PV market for the past two or three decades—the so-called *first-generation PV technology*—is based on thick (150–300 μm) cells of crystalline silicon. Although a mature technology, further innovations and economies of scale may be able to cut the cost of silicon PV electricity by another factor of two or so.

Emerging PV systems based on thin-film layers (1–2 μm) of semiconductor materials—known as the *second-generation PV technology*—are currently competitive with crystalline silicon. Even though modules from these materials are not generally as efficient as those of crystalline silicon, because of the thinness of the material and the ability to use mass production, thin-film PV has the potential to drop PV costs to the aforementioned 6¢/kWh.

Even if thin-film PV meets its long-term potential, according to a report by the Basic Energy Sciences Advisory Committee we would still have to drop costs another three to six times to make it economically attractive enough to provide the scale of applications the world will need. But to achieve such cost reductions we need a quantum leap to a *third-generation PV technology*. This is where nanotechnology comes into the picture. By using nanotechnology, polymer technology, and innovative production techniques, there are two paths whereby nanostructured solar cells can reduce costs sufficiently: by making the solar cells extremely inexpensive, and by making them very efficient at converting sunlight to electricity.

An Inexpensive Route—the Dye-Sensitized Solar Cell

Titanium dioxide (TiO_2) is an inexpensive material that exhibits semiconductor properties. But as a solar cell material, it has a major drawback—its band gap is greater than 3 eV. The solar spectrum, on the other hand, is comprised of photons with energies ranging from 0.3 eV to 3.5 eV. So TiO_2 by itself can absorb and convert only that small portion of the solar spectrum whose photons have an energy equal to or greater than 3 eV. However, scientists from NREL and elsewhere who have worked on this concept have long recognized that TiO_2 has the potential to produce inexpensive electricity by using it in a photoelectrochemical cell with an appropriate dye that can absorb much of the solar spectrum.

The basic design of the cell consists of TiO_2, the dye, and electrolyte sandwiched between a transparent conducting oxide (TCO) electrode and a counter-electrode (see figure). The sunlight excites and oxidizes the dye molecules, which produce electrons that are injected into the conduction band of the titanium dioxide. Charge separation occurs at the interface between the dye molecules and the titanium dioxide. The electrons are transmitted by the TiO_2 to the electrode to provide current for a circuit to do work and return to the cell via the counter-electrode. The oxidized dye molecules are reduced by electrons transferred by redox (oxidation-reduction) couples in the electrolyte.

This concept did not work well until used with TiO_2 nanocrystals of approximately 30 nm diameter. Although these nanocrystals do not exhibit quantization effects, their use greatly increases the contact area between the dye, the TiO_2, and the electrolyte to enhance the efficiency of electron injection from the dye.

One drawback to the concept is that it uses a liquid electrolyte. But this can be circumvented by using a polymer-based electrolyte or a hole-transporting polymer; either alternative leads to longer life and lower cost and provides the ability to make flexible solar cells.

Other alternatives being explored include the use of QDs in place of the dye, or even turning to a different approach altogether—such as a polymer/metal oxide configuration (see the sidebar "Printing Polymer Solar Cells")—to achieve a low-cost solar cell.

Although this approach has not resulted in high-efficiency solar cells—with the best dye-sensitized cells exhibiting efficiencies around 11% and modules having typical efficiencies of about 5%—it has a high potential for low cost because of the low cost of the TiO_2, the dye or the QD alternative, and the polymers and because of inexpensive

by an induced electric field (typically via doping semiconductor layers with extra electrons or holes) to be collected by a transparent conducting oxide layer or a metallic grid. Alternatively, electrons and holes could typically recombine within a few microseconds before they have a chance to be further separated for collection.

In QDs (or nanorods or conjugated polymers), the situation is different. The electron and its associated hole are close together, are not screened from each other, and the coulomb attraction between the two is quite strong (especially in conjugated polymers)—a situation that leads many in the field to label such an electron-hole pair as an "exciton." Under such conditions, the electron-hole pairs in excitons can quickly recombine—typically on a sub-nanosecond time scale. Moreover, excitons retain a neutral charge, so you cannot use an electric field to dissociate them. Rather, excitons in QDs (and conjugated polymers) are dissociated at interfaces with other materials that have high affinities for electrons or holes, with electrons taken in one direction at the interface and holes in another. Movement of excitons is initiated via diffusion; but with a high concentration of excitons and interfaces, this diffusion readily results in dissociation. The dissociation, in turn, sets up a chemical potential gradient that drives the PV effect.

So what can you use to scavenge the excitons and dissociate the charge carriers to produce the chemical gradient and a photocurrent? Both fullerenes (C_{60}) and single-wall carbon nanotubes have high electron affinities that can overcome an exciton's binding energy to siphon freed electrons. Conjugated polymers, in which polymer matrices can be a combination of hole-conducting and electron-conducting can also be used to dissociate and conduct electrons in one direction and holes in another.

processing techniques available for making the cell.

This is also a versatile approach because it will enable us to explore a variety of different substrates on which the cell can be deposited, it could allow production of flexible solar cells that could fit on any surface, and it would allow other layers, such as WO_3, to be added to the device, which would merge the solar-cell function with an electrochromic function. Such a device employing other layers could be used for windows, for example, that would not only generate electricity but would also lighten or darken as desired in accordance with the amount of sunshine.
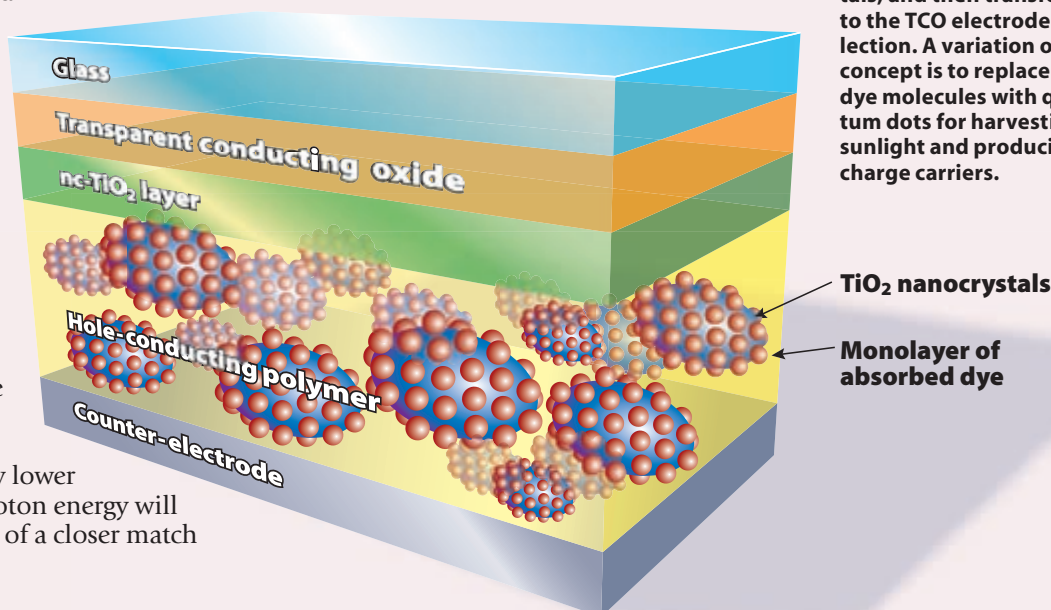
The Road to High Efficiency

Today's typical solar cell relies on a semiconductor material with a single junction and a single band gap. Such a cell has limited efficiency because photons with less energy than the band gap will not be absorbed, while photons with energy greater than the band gap will dislodge electrons into the conduction band, but with too much energy. The excess energy absorbed by an electron will push it into a high and unstable energy level. The electron will quickly relax to a more stable level, emitting the excess energy as heat. This not only wastes the excess photon energy, but the heat it produces further decreases the efficiency of the cell.

One strategy to overcome this limitation is to use several layers of semiconductor materials with different energy band gaps, stacking the layers in decreasing band-gap order. That way, the higher energy photons of the solar spectrum will be absorbed by the higher band gap material and lower energy photons by lower band gap material. Thus, the photon energy will be used more efficiently because of a closer match with the energy band gaps of the absorbing materials, and not so much heat will be produced. By stacking an increasingly large number of materials with different band gaps, as the number of layers approaches infinity you can approach the theoretical efficiency limits of 68% under one sun and 86% under concentration. The problem is that the engineering and physical challenges become increasingly difficult the more layers that are stacked in this manner; and costs rise accordingly. Thus far, the best cell using this approach has been an expensive three-junction device of high-quality material that attained 37.3% efficiency under high solar concentration.

Quantum dots potentially offer a way around this conundrum. Quantum dots can easily be made with different band gaps simply by controlling the size of the dots. By using different-size dots, a many-junction device can be devised to capture and convert the entire solar spectrum. By using a sufficient number of dots with differing sizes, the theoretical limits of efficiency may be approached. And it may be done inexpensively because of the use of colloidal chemistry to produce the QDs and a low-cost matrix in which to imbed them.

The dye-sensitized solar cell represents a pathway toward low-cost solar electricity. It uses dye molecules to absorb a large portion of the solar spectrum and produce electrons, which are injected into the conduction band of the TiO_2 nanocrystals, and then transferred to the TCO electrode for collection. A variation on this concept is to replace the dye molecules with quantum dots for harvesting the sunlight and producing the charge carriers.

Glass

Transparent conducting oxide

nc-TiO_2 layer

Hole-conducting polymer

Counter-electrode

TiO_2 nanocrystals

Monolayer of absorbed dye

Other Uses for NREL Nanotechnology …

There are many other possible uses inherent in NREL's nanotechnology research.

- **Nanocatalysis.** Catalytic reactions occur on catalyst surfaces. Because smaller particles increase surface area, nanocatalysts have the potential for a great amount of surface area to perform catalytic reactions. Other nanostructures (such as nanofibers) can also provide a large active surface area for catalyst support. The modification of electronic and material properties at the nanoscale may also play a beneficial role in catalysis. Nanocatalysis has particular promise for the production of fuels from biomass, producing hydrogen from biogas during the water-gas-shift reaction, and for use with membrane technology for the separation of hydrogen gas.

- **Gas-Separation Membranes.** Gas-separation membranes are used to separate types of gases from one another. This can be accomplished because of the porosity of the membrane materials or because of their ion- or electron-affinity. In either case, nanomaterials, especially those of carbon nanotubes, which have high electron affinity, may offer advantages. Also, because nanostructures offer advantages for catalysis, they can be used to help drive the process of gas separation. Gas separation membranes could find applications in the separation of hydrogen from biogas and in fuel-cell membranes to separate hydrogen protons from the electrons of a hydrogen atom.

# The Right Medium/ The Right Configuration

With QDs, there are immediate barriers to overcome. The first is to dissociate an exciton's freed electron from its paired hole before they recombine. This is done at interfaces with other materials, which will siphon the charge carrier, taking the hole in one direction and the electron in the other to separate grids or collection points (see the sidebar "Excitons").

One way to do this is to deposit the QDs into a medium consisting of a mixture of conjugated polymers (polymers that exhibit semiconductor properties), one of which attracts and conducts holes and the other of which attracts and conducts electrons. This is a highly desired approach because it has the potential to be a very inexpensive alternative, using plastics and colloidal QDs, and it may even allow for high efficiency.

Thus far, however, cell conversion efficiencies using this approach have generally been less than 3%–4%. Difficulties arise with conjugated polymers because they contain many sites that engender the recombination of electrons and holes; the electrons and holes of the induced excitons are strongly attracted to each other and so will quickly recombine; and the charge carriers do not have great mobility and are not quickly dissociated from one another, which increases the probability of recombination. Moreover, the conjugated polymer matrix would have to be blended correctly to ensure that most QDs were in contact with both hole- and electron-conducting polymers, to ensure a high level of exciton dissociation and conduction of charge carriers.

Connecting the Dots

To achieve high-efficiency cells, therefore, it is better not to mix QDs randomly in a polymer blend, but to align the dots in arrays so that they communicate with one another efficiently. This could be done by arraying the dots within a few angstroms of one another to enable electronic coupling among the dots so that electrons can be transported long distances. How you align the dots into arrays becomes the hot question. NREL researchers are exploring a couple of innovative ways to accomplish this: carbon nanotubes and proteins.
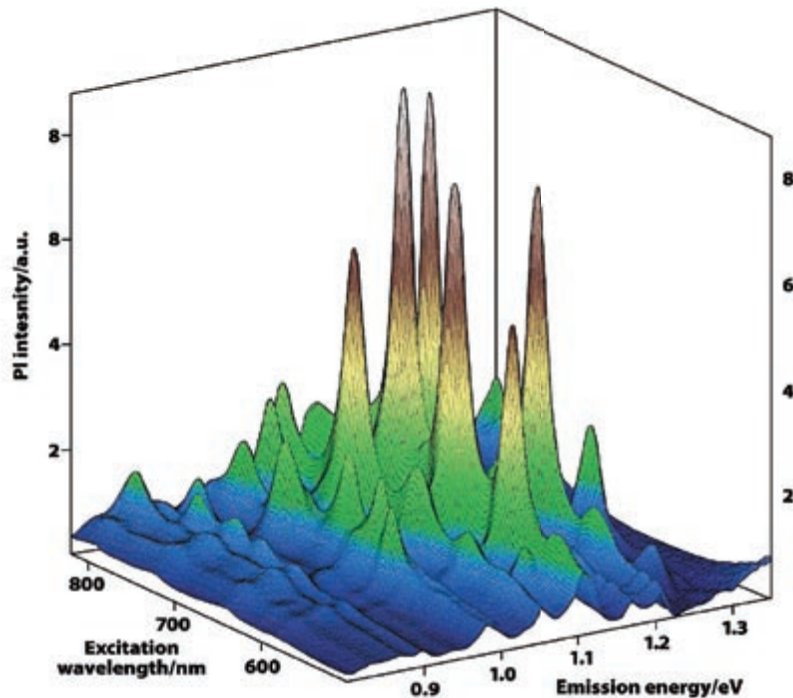
In solution, SWNTs exhibit a photoluminescence spectra whose characteristics differ in accordance with the diameter of the nanotubes and their chirality. Photoluminescence occurs because of the recombination of electrons and holes induced by incident light. Such a spectra is indicative that SWNTs can be used to harvest light to generate electricity.

Carbon Nanotubes. The use of carbon nanotubes for organizing and connecting QDs combines the depth of experience that NREL researchers have with QDs with their expertise with single-wall carbon nanotubes. In this vein of research, scientists are exploring both chemical and physical methods to bring SWNTs and QDs into intimate electronic contact.

With one alternative, NREL researchers have developed a simple way to form one-dimensional close-packed arrays of semiconductor quantum dots. By combining size-selected InP and CdSe QDs and highly pure nanotubes
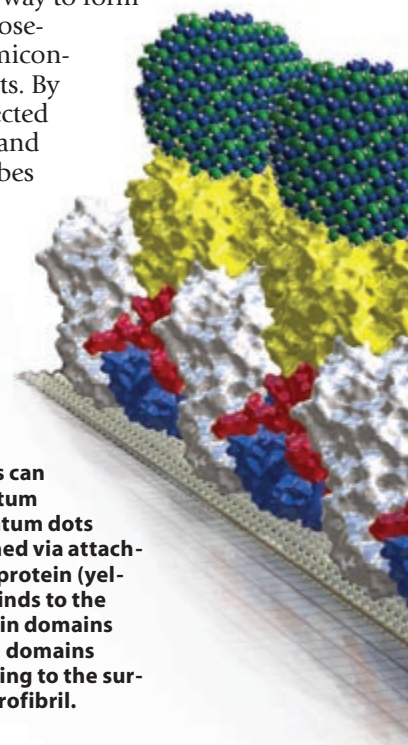
Cellulosome polymers can be used to align quantum dots. Here, CdSe quantum dots (blue-green) are aligned via attachment to a streptactin protein (yellow), which, in turn, binds to the cellulosome via cohesin domains (red). Surface binding domains (blue) are shown binding to the surface of a cellulose microfibril.

that have low defect densities, while gently refluxing both in organic solvents, linear arrays of QDs are self-assembled by van der Waals forces into the grooves between adjacent nanotubes.

In another alternative, SWNTs can be diced into short segments and solubilized in solution using surfactants, much in the same way that semiconductor colloids are typically solubilized. Once in solution, the soluble SWNTs can be treated as reagents and reacted with QDs in solution, to promote coupling among the quantum dots

One interesting characteristic of SWNTs is that they exhibit emission and absorption spectra similar to those shown by QDs of different sizes. In particular, the photoluminescence intensity of the peaks in the spectra is dependent on the diameter of the nanotubes and their chirality (i.e., their helical pitch, or how the graphite sheets roll up). This presents quite a flexibility when using SWNTs with quantum dots. Depending on the type of SWNT used to provide the coupling, the interconnection can either provide simple electronic communication among the dots (when the SWNT is a wire), or it can be used to help harvest the solar spectrum when the SWNT is semiconducting and photoactive. Here, a long-term goal is the construction of hybrid nanoscale systems in which sunlight can be efficiently harvested and converted to generate electricity or fuels, such as hydrogen.
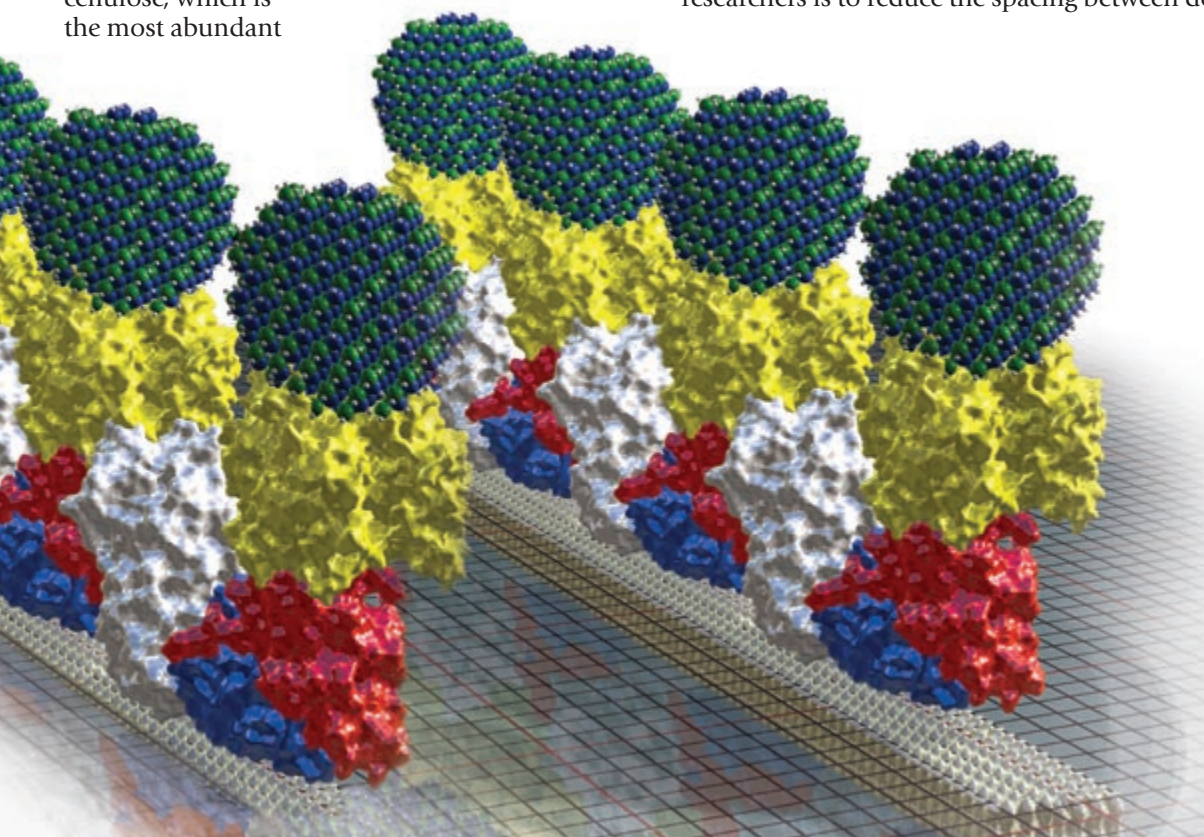
Proteins. The use of proteins to align dots is a method unique to NREL researchers. To be more specific, researchers genetically modify a cellulosome protein polymer so that it will attach to quantum dots. A cellulosome is an intricate multi-enzyme complex that efficiently degrades cellulose, which is the most abundant

organic polymer on the planet. Through the Laboratory's work with biofuels, in which alcohol fuels are derived from biomass cellulose, NREL biochemists have plenty of experience with cellulosomes. Now they are working with NREL physicists to use cellulosomes to align quantum dots.

A cellulosome is a conglomerate of functional subunits. The backbone of this conglomerate is known as the scaffoldin, which organizes and integrates the subunits into a multi-enzyme complex (see figure). The scaffoldin unit contains a site known as the surface-binding domain, which enables the cellulosome to bind to a cellulose substrate. It also holds a series of cohesin domains, to which enzymes will bind via sites on the enzymes known as dockerin domains.

This is the normal order of things. But the size of the cohesin domains where the enzymes normally dock is approximately equal to the size of quantum dots. The trick, therefore, is to remove the enzymes and encourage the cohesin to instead bind to quantum dots or, alternatively, to bind to another protein, which then could bind to quantum dots. Once this is done, and because these units can self-organize into long polymer chains, this approach can be used to produce a chain of quantum dots. Consequently, using an appropriate substrate to which scaffoldin units can adhere, QDs can be maneuvered into arrays with close enough spacing to promote electronic coupling among the dots.

This is breakthrough, state-of-the-art research. Nonetheless, NREL scientists have shown it can be done using a genetically modified cohesin/dockerin polymer to align (CdSe)ZnS QDs on cellulose fibrils. The next challenge for the researchers is to reduce the spacing between dots

from a minimum of 50 Å to about 30–40 Å and to make the spacing more homogeneous.

Hot Carrier Solar Cells

But other breakthrough results may be required to approach the high-efficiency limits of solar cells. One possibility is to develop so-called "hot electron" solar cells. When a freed electron is bumped high into the conduction band by a too-energetic photon, its electronic temperature becomes quite hot (as high as 3,000 K). The hot electron will relax to the bottom of the conduction band, typically within a few hundred femtoseconds, imparting heat to the lattice as it does so.

This can be avoided by removing the hot electron for use in a circuit before it relaxes. Doing so will achieve two things: 1) use of the high-energy electron will increase the photovoltage of the device as well as its efficiency; and 2) the excess energy

will be prevented from heating the device and from lowering its efficiency.

The key to removing the hot electron is to retard its relaxation. And the key to this is to confine the exciton to a quantum dot. A hot electron will cool quickly, especially in the presence of a hole. Remove the hole promptly and, due to quantization effects of a QD, the energy levels to which the electron can readily relax will be limited. The hole can be siphoned in a matter of a few femtoseconds by imbedding the QD in the right material, and perhaps even the right polymer material. This could extend the hot electron relaxation time by one or two orders of magnitude. Combine this with a properly ordered array of QDs, and the hot electrons could be transported along the array via resonant tunneling.

Another way to utilize hot or highly excited electron-hole pairs (excitons) in QDs is to use the
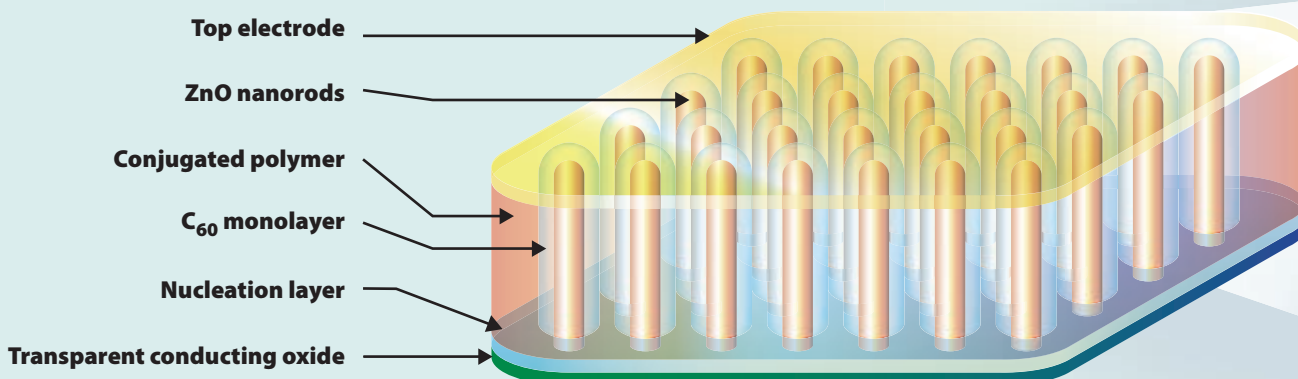
Printing Polymer Solar Cells

NREL scientists are combining the use of nano-, polymer, and low-cost deposition technologies in an approach that promises inexpensive solar cells. The cell concept is innovative. It starts with an inexpensive substrate on top of which is layered a transparent conducting oxide (TCO) that lets light through to the cell and acts as a cell electrode. This TCO layer can be made with nanoparticle precursors to allow constituent materials to be incorporated into an ink that can be written onto the substrate via piezoelectric inkjet printing.

A nucleation layer is then deposited on the TCO. This layer is chemically prepared to enable nanorods to grow vertically (via nucleation in a supersaturated solution) and at close intervals from the surface. The nanorods, which can be of ZnO or other oxides, grow a few nanometers thick and 200 or more nanometers long. This gives the rods a high aspect ratio (i.e., ratio of the rod's length to its width), which, in turn, promotes a great amount of surface area per given mass of material—up to 600 m^2/gm. This gives the nanorods a great ability to scavenge and transport freed electrons from the surrounding material.

Next, the nanorods are coated with a thin layer (less than 20 nm) of conjugated polymer, which absorbs photons to produce excitons. Finally, a silver electrode is deposited on the polymer layer.

Although this is a state-of-the-art concept, NREL researchers have not only successfully fabricated such a device, they are already exploring ways to improve it. One way is to coat the nanorods with a monolayer of a material that has high electron affinity, such as fullerenes (C_{60}), before the conjugated polymer is applied. In conjugated polymers, photon-induced excitons have low mobility and the electron and hole can typically recombine on a sub-nanosecond time scale. That is why C_{60} (or some other material with high electron affinity) would be valuable in such a device; it could quickly dissociate excitons and extract electrons from the polymer and transfer them to the ZnO nanorods, which would conduct the electrons to the TCO. This would enable the conjugated polymer to conduct the dissociated holes to the silver contacts.

The device can be designed so that excitons will travel only 5–20 nm before encountering an interface. This

Top electrode

ZnO nanorods

Conjugated polymer

C_{60} monolayer

Nucleation layer

Transparent conducting oxide

excess energy to create multiple electron-hole pairs. NREL researchers have found that up to three excitons per photon can be created in small band gap semiconductor QDs when the photon energy is four times the QD band gap. This approach is very promising for creating much more efficient nanocrystalline solar cells.

The exploitation of hot electrons is just one of the cutting-edge nanotechnology concepts being explored by NREL researchers. But breakthroughs in this area, along with continued advances in QDs, nanorods, carbon nanotubes, conjugated polymers, and other related fields discussed here have the potential not only to present the world with inexpensive renewable electricity, but also to provide it with plentiful non-carbon energy in all usable forms—for transportation; building heating, cooling, and lighting; and industrial processing needs.

For More Information

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enhances the ability of electrons and holes to be separated more quickly than they may recombine. By designing a device in which electrons and holes are separated at interfaces in a few tens of femtoseconds (10^{-15} seconds) or less, charge carriers are efficiently collected to produce an electric current.

Such a concept has great potential. Researchers believe, for example, that there may be the possibility that much of the device—the TCO, the fullerenes, the polymer, and the silver electrode—could be deposited via inkjet printing. Also, because conjugated polymers may be chemically altered to exhibit different absorption characteristics, there is the potential that they could be tuned to absorb the entire solar spectrum to produce carriers. One way of doing this is to chemically tune the band gap by modifying the conjugated polymer backbone. Another way is to attach side chemical groups to the polymer backbone.

Effectively, each nanorod/C_{60}/polymer combination can be considered a minicell, connected to the silver electrode on one end and to the TCO electrode on the other. This opens the door for tuning each minicell combination to different wavelengths of light. Thus, a cell like this could become a many-junction device that could efficiently absorb and convert the entire solar spectrum to excitons.

Such a solar cell would have many advantages. The entire cell, for example, would be approximately 200 nm thick and would thus use very little material. It could be made on an inexpensive and flexible substrate to fit surfaces as needed. There is the possibility that almost the entire structure could be made using solution chemistry, nanoprecursor inks, and inkjet printing. The entire device could be processed at temperatures below 400°C, and probably at less than 200°C—both of which are far lower than the temperatures at which solar cell are currently processed. The device could be made without using vacuum technology, using much less expensive equipment. And it could be made translucent, for use on such spaces as windows to allow lighting and to produce electricity. All of this could add up to the potential for an extremely inexpensive solar cell and affordable electricity.
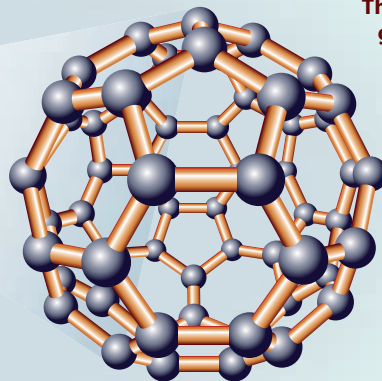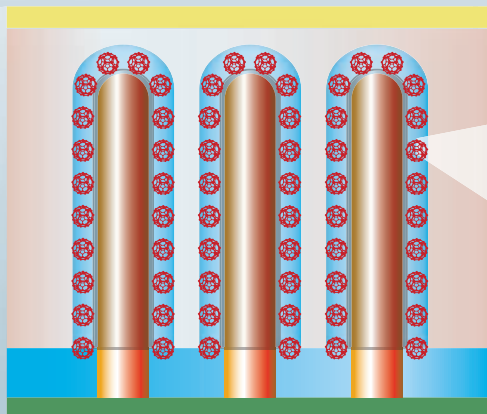
This solar cell concept uses conjugated polymer to harvest light and produce excitons, C_{60} to dissociate electrons from the excitons, ZnO nanorods to transport the electrons to the TCO electrode, and hole-conducting polymer to carry holes to the silver electrode. With the potential for tuning the cell to absorb and convert much of the solar spectrum and to inkjet print much of the cell, this approach could result in very inexpensive electricity.